CHEMISTRY
A EUROPEAN JOURNAL

From a Monomer to a Protein-Sized, Doughnut-Shaped Coordination Oligomer—The Influence of Side Chains of C_3-Symmetric Ligands in Supramolecular Chemistry

Iris M. Müller,* Daniela Möller, and Kirsten Föcker[a]

Abstract: Herein we describe the importance of side chains in C_3-symmetric ligands in supramolecular chemistry. The reaction of the new ligand tris(5-bromo-2-methoxybenzylidene)triaminoguanidinium chloride $[\mathrm{H}_3Me_3Br_3L]\mathrm{Cl}$ (**1**) with ZnCl_2 results in the formation of the monomeric complex $(\mathrm{Et}_3\mathrm{NH})_2[(\mathrm{ZnCl}_2)_3Me_3Br_3L]$ (**2**), in which the ligand remains in a conformation less favourable for the coordination of metal centres. The use of the related tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride, $[\mathrm{H}_6Br_3L]\mathrm{Cl}$, under similar conditions, results in the formation of two different dimeric compounds $(\mathrm{NH}_4)[\{[\mathrm{Zn}(\mathrm{NH}_3)]_3Br_3L\}_2\{\mu\text{-}(\mathrm{OH})\}_3]\cdot\frac{1}{4}\mathrm{MeOH}$ (**3**) and $[\mathrm{Zn}\{\mathrm{Zn}_2(\mathrm{OH}_2)_3(\mathrm{NH}_3)Br_3L\}_2]$ (**4**), depending on the solvent mixture used. The comparable reaction of the ligand tris(5-bromo-2-hydroxy-3-methoxybenzylidene)triaminoguanidinium chloride $[\mathrm{H}_6(OMe)_3Br_3L]\mathrm{Cl}$ (**5**), leads to the formation of a doughnut-shaped, protein-sized coordination oligomer $(\mathrm{Et}_3\mathrm{NH})_{18}[\{\mathrm{Zn}[\mathrm{Zn}_2\mathrm{Cl}\{(OMe)_3Br_3L\}]_2\}_6(\mu\text{-}\mathrm{Cl})_6(\mathrm{OH}_2)_6]\cdot x\,\mathrm{CH}_3\mathrm{CN}$ (**6**), which comprises six dimeric $[\mathrm{Zn}_5\{(OMe)_3Br_3L\}_2]$ units. Whereas **3** and **4** decompose in DMSO solution, **6** is surprisingly stable in the same solvent.

Keywords: ligand design · supramolecular chemistry · tridentate ligands · zinc

Introduction

The rapidly growing field of supramolecular coordination chemistry can be divided into two classes by the formed products, namely polymers and discrete cage molecules. The polymers are well known because of the possible applications of such compounds as new materials, heterogeneous catalysts, and ion exchangers.[1] The rational design of discrete cage molecules can be carried out by following the molecular library method,[2] in which the stochiometry and symmetry elements of the product are predestined by the molecular starting fragments. Up to now, in most cases using this design strategy cages have been formed with the metal centres representing the corners, which are linked by twofold bridging ligands that represent the edges. The use of ligands covering the faces of the cage is much more scarce, and even then often only a small part of the face is covered, which leads, for example, for triangular units to the formation of adamantanoid instead of tetrahedral coordination cages with wide openings at the corners.[3]

We previously reported the metal binding properties of tris(2-hydroxybenzylidene)triaminoguanidinium chloride $[\mathrm{H}_6L]^+$ (Scheme 1a) and its use as a tris-chelating ligand with threefold symmetry.[4] This ligand could be used to form coordination cages with the outer shape of a tetrahedron and the formula $[\{(\mathrm{CdCl})_3L\}_4]^{8-}$,[5] and even with the outer shape of an octahedron and the formula $[(\mathrm{Pd}_3L)_8\{\mu\text{-}(bar)\}_{12}]^{16-}$.[6]

The structural characterisation of large cage compounds by X-ray crystallography is often difficult due to rapid solvent loss and a typical high degree of disorder of both counterions and solvent molecules. We were able to increase the scattering power of the ligands by the introduction of heavy atoms, in this way we synthesised the new ligand tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride, $[\mathrm{H}_6Br_3L]^+$, (Scheme 1b).[7] This can also be used to build a molecular tetrahedron under similar conditions to those applied previously ($[\{(\mathrm{CdCl})_3Br_3L\}_4]^{8-}$).[8] But there is one important difference between the two coordination cages $[\{(\mathrm{CdCl})_3L\}_4]^{8-}$ and $[\{(\mathrm{CdCl})_3Br_3L\}_4]^{8-}$. While the first one can only be formed in the presence of a tetrahedral counter cation small enough to be encapsulated, the second one can also be formed in absence of tetrahedral cations, providing

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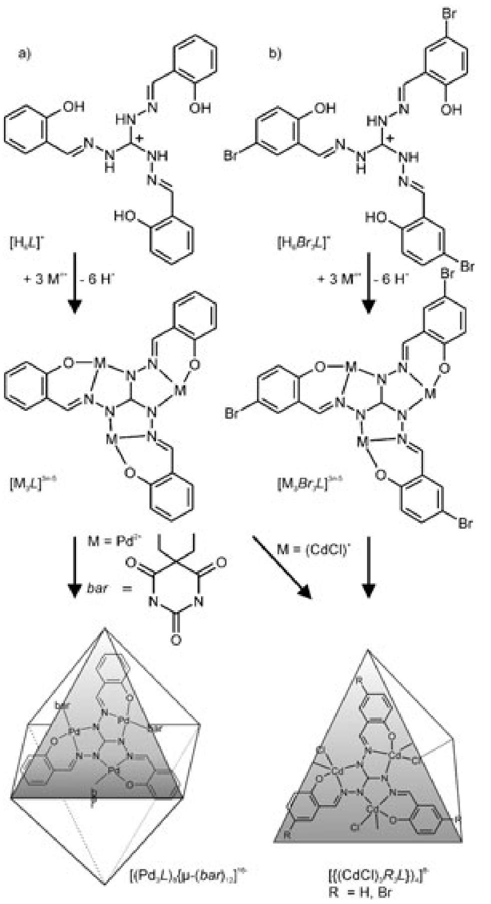
DOI: 10.1002/chem.200401260



Scheme 1. C_3-symmetric ligands as triangular building blocks, and known closed coordination cages formed by these ligands.[5,6,8]

that other cations and solvent molecules are available to fill the inner space. Owing to the steric influence of the bromine atoms the capsule is closed more tightly.

Herein we describe more derivatives of $[H_6L]^+$ and their use for the coordination of Zn^{2+} ions. The resulting complexes (a monomeric and two dimeric species, as well as a protein-sized cyclic oligomer) demonstrate the importance of the side chain.

Results and Discussion

To date the coordination cages formed by C_3-symmetric ligands were highly charged, therefore the first new ligand we present here is tris(5-bromo-2-methoxybenzylidene)triaminoguanidinium chloride $[H_3Me_3Br_3L]Cl$, (**1**), which should form $[M_3Me_3Br_3L]^{3n-2}$ triangular building blocks, and result in cage compounds with lower charge. $[H_3Me_3Br_3L]Cl$ can easily be obtained from a Schiff base reaction of 5-bromo-2-methoxybenzaldehyde and triaminoguanidinium chloride. As the other ligands of this class, the $[H_3Me_3Br_3L]^+$ ion can adopt two different conformations (Figure 1a). In solution conformation 2 is predominant, which is less favourable for the coordination of metal centres. In a $^1H,^1H$ NOESY experiment of **1** in $[D_6]DMSO$ no cross peak between H-C$_{(6)}$ and H-C=N was observed. This behaviour has been observed for other ligands of this class, and the conformation of the ligands usually change readily on metalation of their N and O atoms.[4,7]

The reaction of $[H_3Me_3Br_3L]Cl$ with $ZnCl_2$ in acetone in the presence of Et_3N as base results in the formation of

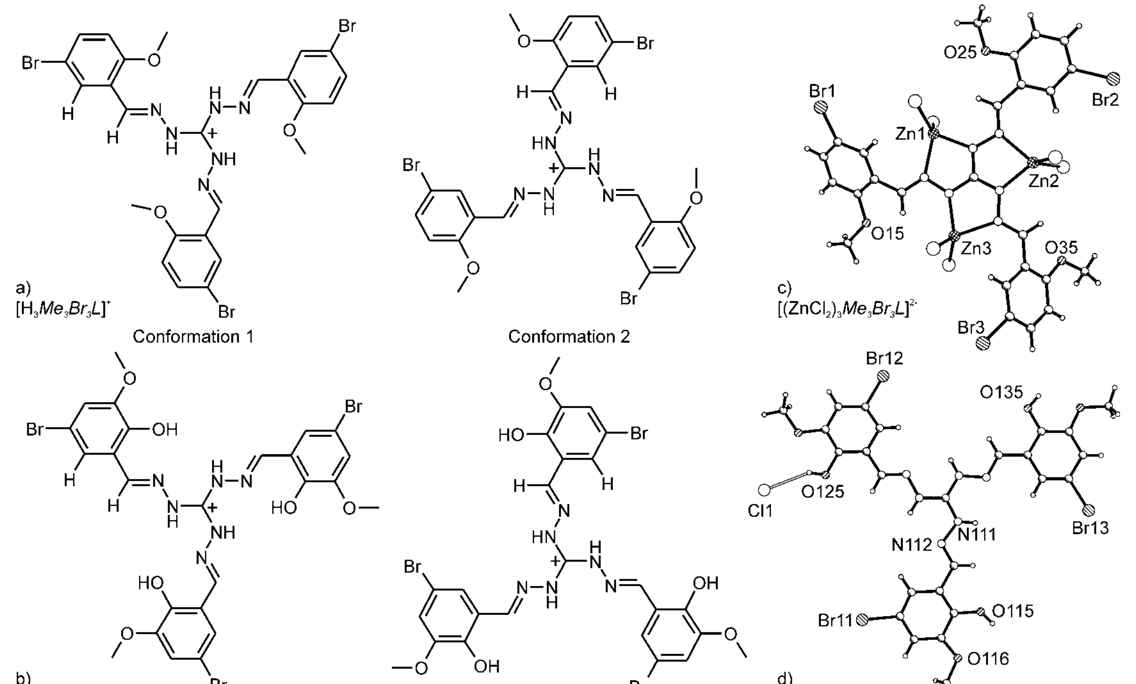


Figure 1. possible conformations of the new ligands: a) $[H_3Me_3Br_3L]^+$ (**1**), b) $[H_6(OMe)_3Br_3L]^+$ (**5**). Crystal structures of c) $[(ZnCl_2)_3Me_3Br_3L]^{2-}$ (**2**; counter cations omitted for clarity) and d) $[H_6(OMe)_3Br_3L]Cl$ (**5**).

Table 1. Selected bond lengths [Å] and angles [°] of $[H_6Br_3L]^+$,[4] and the compounds **2**–**6**.

	$[H_6Br_3L]^+$	**5**	**2**	**3**	**4**	**6**
C−N1	1.336(2)	1.334(6)	1.350(9)	1.35(1)	1.35(3)	1.36(4)
N1−N2	1.389(3)	1.39(1)	1.394(8)	1.38(1)	1.38(2)	1.38(3)
N2=C	1.278(3)	1.28(1)	1.29(1)	1.29(1)	1.29(2)	1.29(2)
C−O	1.348(4)	1.36(1)	1.36(1)	1.31(1)	1.32(3)	1.36(2)
C−Br	1.906(3)	1.90(1)	1.91(1)	1.90(1)	1.90(2)	1.89(2)
N1-C-N1	120.0(1)	120(1)	120.0(6)	120.0(8)	120(2)	120(2)
C-N1-N2	117.4(2)	117(1)	115.1(8)	113.1(6)	113(1)	112(2)
C-N1-Zn	–	–	113.7(5)	113.9(7)	114(1)	112(2)
N2-N1-Zn	–	–	131(1)	132.5(7)	131(2)	133(2)
N1-N2=C	115.1(2)	115(1)	115.3(9)	117(1)	116(2)	116(2)
C=N2-Zn	–	–	133(2)	126.6(5)	126(2)	127(2)
N1-N2-Zn	–	–	111.3(8)	116(1)	117(2)	116(2)
C-O-C	–	117.0(7)	118(2)	–	–	118(2)
C-O-Zn	–	–	–	129(1)	128(2)	123(4)

bright yellow crystals of $(Et_3NH)_2[(ZnCl_2)_3Me_3Br_3L]$ (**2**). To our surprise the X-ray analysis of **2** showed that no change in the conformation had occurred. The triply deprotonated ligand bonds to three $ZnCl_2$ units in a chelating manner, and the methoxy groups are not involved in the coordination (Figure 1c). The observed bond lengths and angles fall within the expected ranges; the central C−N bond (1.350(9) Å) is significantly shorter than a C−N single bond (1.469 Å),[9] in accordance with the partial double-bond character (Table 1). The Zn^{2+} centres adopt distorted tetrahedral coordination geometries with observed angles at the metals of 79.6(6) to 118(2)° (Table 2). To see whether this tetrahedral coordination geometry forces the system to adopt this coordination mode we performed a similar reaction with the ligand $[H_6Br_3L]Cl$, which has already been shown to change its conformation in the presence of base or Cd^{2+} ions.[7,8] The reaction of $[H_6Br_3L]Cl$ with $ZnCl_2$ in a mixture of DMF, water and methanol in the presence of NH_3 as base results in the formation of orange-red crystals of a dimeric complex $(NH_4)[\{\{Zn(NH_3)\}_3Br_3L\}_2\{\mu\text{-}(OH)\}_3]\cdot{}^1/_4MeOH$ (**3**). The result of the X-ray structure analysis is shown in Figure 2. Two triangular $[\{Zn(NH_3)\}_3Br_3L]^+$ units are orientated parallel to each other, with the Zn^{2+} centres being linked by bridging OH^- groups.

In **3**, the ligand adopts the favourable conformation for the complexation of metals, and the Zn^{2+} centres exhibit distorted trigonal-bipyramidal coordination spheres with both axial and one equatorial position occupied by the ligand. Each $[\{Zn(NH_3)\}_3Br_3L]^+$ unit is chiral, as best appreciated in the screw direction of the central CN_6 core. Both triangular

Table 2. Selected bond lengths [Å] and angles [°] at the Zn^{2+} centres (tetrahedral in **2**, trigonal bipyramidal **3**, **4**, **6**).

	2	**3**	**4**	**6**
Zn−N1	2.00(1)	2.09(2)	2.09(2) 2.18(4)[a]	2.06(2) 2.20(5)[a]
Zn−N2	2.092(8)	2.08(2)	2.08(3) 2.14(2)[a]	2.10(3) 2.13(3)[a]
$Zn-O^L$	–	2.06(2)	2.06(2) 2.09(3)[a]	2.11(6) 2.10(1)[a]
$Zn-OH_2$	–	–	2.07(3)	2.01(3)
$Zn-NH_3$	–	2.11(2)	2.15(8)	–
Zn−Cl	2.22(1)	–	–	2.25(1)
Zn−(μ-Cl)	–	–	–	2.38(1)/2.48(1)
Zn−(μ-OH)	–	1.98(1)	–	–
$Zn-(\mu\text{-}O^L)$	–	–	–	2.05(2)
N1-Zn-N2	79.6(6)	76.3(5)	76.0(4) 73.5(3)[a]	76.6(9) 73.0(8)[a]
$N1\text{-}Zn\text{-}O^L$	–	161(2)	161(2) 156(3)[a]	157(5) 155(1)[a]
$N2\text{-}Zn\text{-}O^L$	-	86.7(9)	87(1) 86(2)[a]	84(2) 83(1)[a]
N2-Zn-L′	114(2)	119(2)	118(4)	117(2)–126(2)
N2-Zn-L″	–	130(3)	129(4)	125(3)–154(2)
L′-Zn-L″	118(2)	111(3)	112(4)	82(1)–117(2)

[a] Octahedral Zn^{2+}.

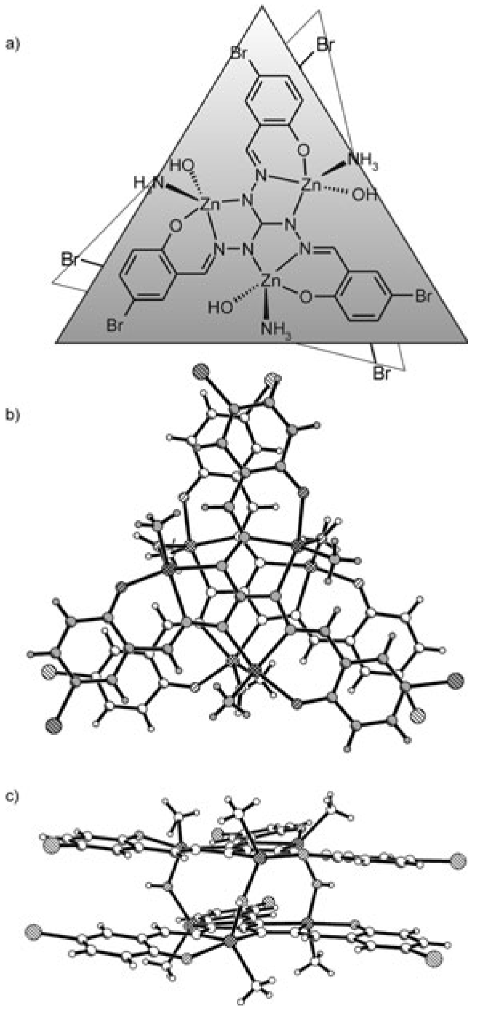


Figure 2. $[\{\{Zn(NH_3)\}_3Br_3L\}_2\{\mu\text{-}(OH)\}_3]^-$ (**3**; counter cation and disorder omitted for clarity). a) schematic drawing, b) crystal structure in the same orientation, c) side view.

units in a dimer exhibit the same chirality, leading to a chiral complex. In this way a close Br···Br contact can be avoided. Both enantiomers are found in the same unit cell, as **3** crystallizes in the centrosymmetric space group $R\bar{3}$. The ligand undergoes no further distortion due to the metalation, and all bond lengths and angles fall within the expected ranges (Table 1). Complex **3** exhibits disorder with one Zn centre being twisted out of the triangular plane at an occupancy of 0.25. Instead of being bonded to the bridging OH^- group it bonds to a methanol molecule (d(Zn···O) = 2.359(2) Å). It remains distorted trigonal bipyramidally coordinated but this time two equatorial and one axial position are occupied by the ligand, and the other axial position is taken by the NH_3 coligand.

If the same reaction is performed in the absence of methanol, the formation of yellow crystals of $[Zn\{Zn_2(OH_2)_3(NH_3)\mathit{Br_3L}\}_2]$ (**4**) is observed. This is again a dimeric complex, but this time there are two different types of Zn^{2+} centres. One of them (Zn12, Figure 3) adopts a distorted octahedral coordination geometry and bonds two $[\mathit{Br_3L}]^{5-}$ units with a *trans* angle of 170(1)°. In addition, each ligand coordinates two Zn^{2+} centres with distorted trigonal-bipyramidal geometry, occupying the two axial and one equatorial position. The four remaining coordination sites are taken by water and ammonia molecules.

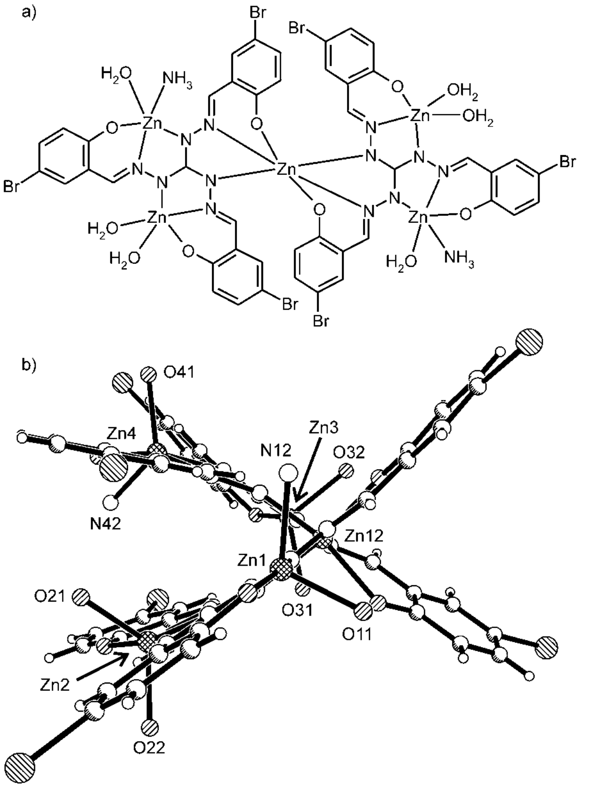


Figure 3. $[Zn\{Zn_2(OH_2)_3(NH_3)\mathit{Br_3L}\}_2]$ (**4**; protons of the coordinated H_2O and NH_3 molecules omitted for clarity). a) schematic drawing, b) crystal structure.

The bond lengths and angles observed for all the Zn centres in **4** remain effectively unchanged compared to those in **2** and **3** (Table 2). Each ligand coordinates in this way three metal atoms and remains undistorted. Again the complete dimeric complex is chiral and both enantiomers can be found in the unit cell (centrosymmetric space group $P\bar{1}$).

To obtain information about possible reactions from one dimeric species to another, we studied their stability in solution. Both compounds exhibit very low solubilities in common solvents, but in [D$_6$]DMSO we were able to dissolve sufficient quantities to allow ^{1}H NMR experiments. To our surprise both spectra were identical, with that of **4**, as an example, being depicted in Figure 4a. Only a few signals are observed, indicating that the compound formed in solution exhibits high symmetry. The observed chemical shifts are different than the ones measured for protonated $[H_6\mathit{Br_3L}]^+$,[7] so it seems reasonable to assume that a $[Zn_3\mathit{Br_3L}]^+$ species has been formed. The free coordination sites at the metals should be occupied by water and/or ammonia molecules. No change in the chemical shift of the other organic solvents present (methanol, DMF and DMSO) is observed.

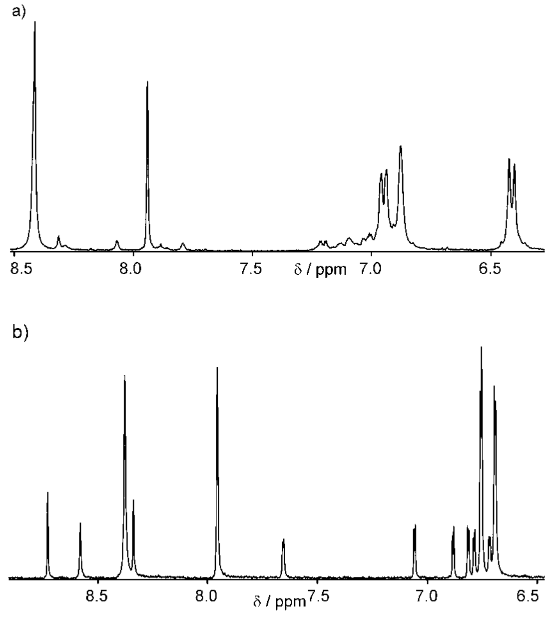


Figure 4. ^{1}H NMR spectra (400 MHz, [D6]DMSO, 22 °C): a) $[Zn\{Zn_2(OH_2)_3(NH_3)\mathit{Br_3L}\}_2]$ (**4**), b) $(Et_3NH)_{18}[\{Zn\{Zn_2(Cl)\mathit{(OMe)_3Br_3L}\}_2\}_6(\mu\text{-}Cl)_6(OH_2)_6]$ (**6**).

We were able to demonstrate so far that the side chain at the ligand has an important influence on the resulting products with Zn^{2+}. The exchange of a hydroxyl group by a methoxy group led to the ligand being unable to change its conformation into the one favourable for the coordination of metal centres. Whereas the reaction of $[H_6L]^+$ with Zn^{2+} leads to the formation of a monomeric $[\{Zn(NH_3)(OH_2)\}_3L]^+$ species,[4] the introduction of a heavy atom in the 5-position leads to the formation of two different dimeric species **3** and **4** in which the zinc atoms exhibit different environments.

To combine both influences in one ligand, we decided to synthesise the new ligand tris(5-bromo-2-hydroxy-3-methoxybenzylidene)triaminoguanidinium chloride $[H_6\text{-}\mathit{(OMe)_3Br_3L}]Cl$ (**5**; Figure 1b). As for the other ligands of this class, **5** can adopt two conformations, with the one less favourable for the coordination of metals being found in the solid state (Figure 1d). Again we performed $^1H,^1H$ NOESY experiments and this time a strong cross peak between H-C=N and $H\text{-}C_{(6)}$ is observed, indicating that in $[D_6]$DMSO solution the favourable conformation 1 is already predominant.

Encouraged by this result we allowed **5** to react with Zn^{2+} in a mixture of acetonitrile and DMF in the presence of Et_3N. After two weeks, yellow crystals of $(Et_3NH)_{18}[\{Zn[Zn_2Cl\{\mathit{(OMe)_3Br_3L}\}]_2\}_6(\mu\text{-}Cl)_6(OH_2)_6]\cdot x\,CH_3CN$ (**6**) were formed. The crystal structure of the protein-sized cyclic coordination oligomer **6** with a diameter of 3.2(1) nm is shown in Figure 5.

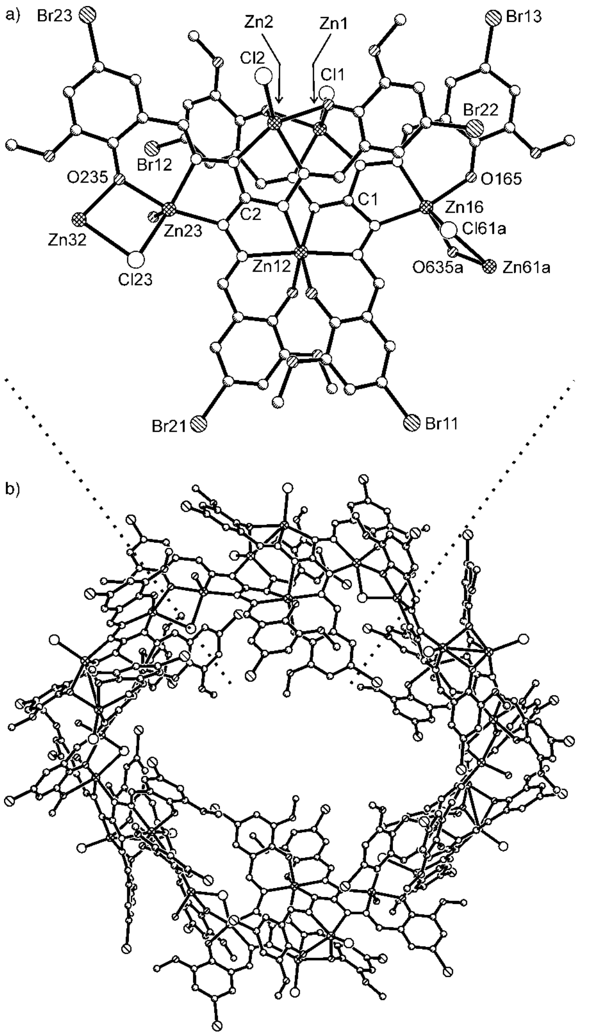


Figure 5. $[\{Zn[Zn_2Cl\{\mathit{(OMe)_3Br_3L}\}]_2\}_6(\mu\text{-}Cl)_6(OH_2)_6]^{18-}$ (**6**; counter cations and protons omitted for clarity). a) dimeric building unit, b) complete ring formed by six dimeric units.

The ring is formed by six dimeric units (space group $P\bar{1}$). Adoption of a higher symmetry is apparently prohibited due to the torsion of the dimers relative towards one other. Each dimeric unit is related to that found in **4**. Again one central Zn^{2+} ion (Zn12, Figure 5) is coordinated in a distorted manner by two $[\mathit{(OMe)_3Br_3L}]^{5-}$ units with *trans* angles of 174(1)°. Each ligand bonds two additional metal ions by occupying both axial and one equatorial positions (Zn1 & Zn16 or Zn2 & Zn32 respectively) in their distorted trigonal-bipyramidal coordination spheres. But in this case two Zn atoms come into close contact with one other (Zn1 and Zn2) at an observed distance of 3.043(6) Å. These two metal atoms are linked by two phenolate oxygen atoms of the ligands, leading to the formation of a four-membered ring. The fifth coordination site is occupied by Cl^- coligands. Two further metal ions (Zn16 and Zn23) in each dimeric unit participate in the linkage to neighbouring dimers by one bridging phenolate oxygen (Figure 5, O235 and O635a, respectively) and one bridging Cl^- ion (Cl23 and Cl61a, respectively). The remaining coordination site at Zn23 is occupied by a water molecule. The observed bond lengths and angles in the ligand as well as at the metal centres remain nearly unchanged, only the distortion at some of the trigonal-bipyramidal Zn^{2+} centres becomes more pronounced. The complete doughnut-shaped ring (Figure 6) contains thirty Zn^{2+} ions, twelve $[\mathit{(OMe)_3Br_3L}]^{5-}$ ligands, eighteen Cl^- coligands and six water molecules, leading to an overall charge of 18−. Of the expected eighteen Et_3NH^+ counter cations, only twelve could be located and refined in the X-ray structure analysis and are hydrogen-bonded to the phenolate oxygen atoms of the twelve ligands (one to each) with an observed N···O distance of 2.72(6) Å. The remaining six Et_3NH^+ ions are located outside the ring and disordered with acetonitrile and water molecules.

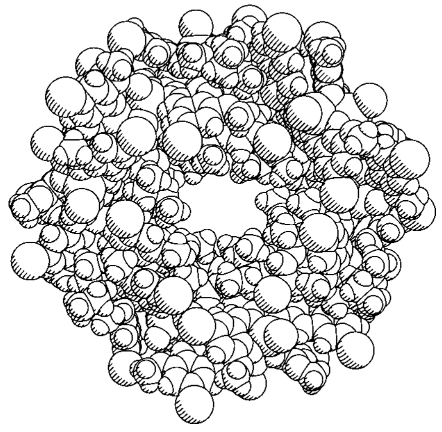


Figure 6. Space-filling drawing of **6**, including the twelve hydrogen-bonded Et_3NH^+ ions.

Complex **6** exhibits sufficient solubility in $[D_6]$DMSO to allow a ^1H NMR experiment to be run. The most interesting part of the spectrum is depicted in Figure 4b. In the range $\delta = 8.7\text{–}8.3$ ppm four singlets with intensities of 4+4+24+

$4 = 36$ H can be found, which fit to the H-C=N protons of twelve ligands. In addition to the signal of DMF ($\delta = 7.95$ ppm)[10] eight sets of doublets ($^4J \sim 2$ Hz) can be found from $\delta = 7.7$ to 6.6 ppm with intensities of $4+4+4+4+4+24+4+24 = 72$ H, corresponding to the aromatic protons (H-$C_{(4)}$ & H-$C_{(6)}$) of twelve ligands. Two signals for the methoxy groups can be seen ($\delta = 3.8$ ppm, 12 H and $\delta = 3.7$ ppm, 96 H), and the number of protons is in accordance with that expected for twelve $[(OMe)_3Br_3L]^{5-}$ units. The high number of different signals suggests that the cyclic oligomer remains unchanged in solution. The charge could also be confirmed by the number of CH_2 protons ($\delta = 2.8$ ppm, ~110 H, expected $108 = 18 \times 3 \times 2$) and CH_3 protons ($\delta = 1.2$ ppm, ~160 H, expected $162 = 18 \times 3 \times 3$) for the Et_3NH^+ counter cations.

In conclusion, we were able to show the importance of side chains in C_3-symmetric ligands for supramolecular chemistry, which are seemingly not involved in coordination nor have any obvious steric influence. The use of $[Me_3Br_3L]^{2-}$ and $[Br_3L]^{5-}$ for the coordination of Zn^{2+} ions results in the formation of a monomeric (**2**) and two dimeric species (**3**, **4**), respectively. Analogous reactions with a new ligand combining both side chain influences ($[(OMe)_3Br_3L]^{5-}$, **5**) led to the formation of a doughnut-shaped and protein-sized coordination oligomer **6** built up of six dimeric units. Whereas compounds **3** and **4** undergo decomposition in DMSO solution, the ring anion of **6** shows surprisingly high stability in the same solvent.

Experimental Section

Tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride $[H_6Br_3L]Cl$ was prepared by literature methods.[7]

$[H_3(C_{25}H_{21}N_6O_3Br_3)]Cl$ (1): Triaminoguanidinium chloride (2.3928 g, 0.017 mol) was dissolved in a hot mixture of ethanol (54 mL) and water (27 mL). A solution of 5-bromo-2-methoxybenzaldehyde (10.8561 g, 0.0505 mol) in ethanol (180 mL) was slowly added. The resulting suspension (pH ~ 3) was allowed to cool to room temperature. The precipitate of tris(5-bromo-2-methoxybenzylidene)triaminoguanidinium chloride (**1**) was collected, washed with acetone (100 mL) and dried under reduced pressure. Yield: 10.63 g (0.015 mol, 89.1 %). Elemental analysis calcd (%) for $C_{25}H_{24}N_6O_3Br_3Cl \cdot 2H_2O \cdot 0.5(CH_3)_2CO$ (796.73): C 39.95, H 3.92, N 10.55; found: C 40.05, H 4.17, N 10.57; ^{1}H NMR (400 MHz, $[D_6]$DMSO, 22 °C): $\delta = 12.28$ (s, 3 H; N-H), 9.02 (s, 3 H; H-C=N), 8.46 (d, ^4J(H,H) = 3.0 Hz, 3 H; H-$C_{(6)}$), 7.64 (dd, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 3.0 Hz, 3 H; H-$C_{(4)}$), 7.14 (d, ^3J(H,H) = 9.0 Hz, 3 H; H-$C_{(3)}$), 3.91 ppm (s, 9 H; OCH_3); ^{13}C NMR (100 MHz, $[D_6]$DMSO, 22 °C): $\delta = 157.21$ ($C_{(2)}$), 148.74 (C^+), 145.01 (C=N), 134.70 ($C_{(4)}$), 128.58 ($C_{(6)}$), 122.86 ($C_{(1)}$), 114.20 ($C_{(3)}$), 112.53 ($C_{(5)}$), 55.98 ppm (OCH_3).

$(C_6H_{16}N)_2[(ZnCl_2)_3(C_{25}H_{21}N_6O_3Br_3)]$ (2): Dry zinc chloride (20.8 mg, 0.15 mmol) and tris(5-bromo-2-methoxybenzylidene)triaminoguanidinium chloride (36.9 mg, 0.050 mmol) were dissolved in acetone (1.5 mL). Triethylamine (0.5 mL) was added. After a couple of hours yellow crystals of **2** were formed. Yield: 56.7 mg (0.043 mmol, 86.0 %). Elemental analyses calcd (%) for $C_{37}H_{53}N_8O_3Br_3Zn_3Cl_6$ (1306.47): C 34.02, H 4.09, N 8.58; found: C 34.02, H 4.38, N 8.52; ^{1}H NMR (400 MHz, $[D_3]CH_3CN$, 22 °C): $\delta = 8.75$ (s, 3 H; H-C=N), 8.52 (d, ^4J(H,H) = 2.0 Hz, 3 H; H-$C_{(6)}$), 7.59 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 3 H; H-$C_{(4)}$), 7.01 (d, ^3J(H,H) = 8.5 Hz, 3 H; H-$C_{(3)}$), 3.93 (s, 9 H; OCH_3), 3.12 (q, ^3J(H,H) = 7.0 Hz, 12 H; CH_2 Et_3NH^+), 1.25 ppm (t, ^3J(H,H) = 7.0 Hz, 18 H; CH_3 Et_3NH^+); ^{13}C NMR (100 MHz, $[D_3]CH_3CN$, 22 °C): $\delta = 158.78$ ($C_{(2)}$), 148.23 (C^+), 144.89 (C=N), 135.68 ($C_{(4)}$), 131.24 ($C_{(6)}$), 123.97 ($C_{(1)}$), 114.50 ($C_{(3)}$), 113.73 ($C_{(5)}$), 57.15 (OCH_3), 47.97 (CH_2 (Et_3NH^+)), 9.33 ppm (CH_3 (Et_3NH^+)).

$(NH_4)[\{\{Zn(NH_3)\}_3(C_{22}H_{12}N_6O_3Br_3)\}_2(\mu\text{-}OH)_3(CH_3OH)_{0.25}]$ (3): Tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride (71.8 mg, 0.10 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF) (2 mL). This solution was added to a suspension of dry zinc chloride (85.4 mg, 0.63 mmol) in DMF (2 mL). Water (1.4 mL) and methanol (0.2 mL) were added. After slow diffusion of ammonia gas into the reaction mixture, orange-red crystals of **3** were formed. Yield: 22.3 mg (0.012 mmol, 24.0 %). Elemental analyses calcd (%) for $C_{44}H_{49}N_{19}O_9Zn_6Br_6 \cdot 22CH_3OH$ (2564.67): C 30.91, H 5.38, N 10.38; found: C 30.93, H 3.34, N 10.46; ^{1}H NMR (400 MHz, $[D_6]$DMSO, 22 °C): $\delta = 8.41$ (s, 1 H; H-C=N), 6.94 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.0 Hz, 1 H; H-$C_{(4)}$), 6.87 (d, ^4J(H,H) = 2.0 Hz, 1 H; H-$C_{(6)}$), 6.41 (d, ^3J(H,H) = 8.8 Hz, 1 H; H-$C_{(3)}$).

$[Zn\{Zn_2(OH_2)_3(NH_3)(C_{22}H_{12}N_6O_3Br_3)\}_2]$ (4): Tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride (67.6 mg, 0.098 mmol) was dissolved in DMF (2 mL). This solution was added to a suspension of dry zinc chloride (40.2 mg, 0.30 mmol) in DMF (2 mL). Water (0.7 mL) was added. After slowly diffusion of ammonia gas into the reaction mixture yellow crystals of **4** were formed. Yield: 26.3 mg (0.015 mmol, 30.6 %). Elemental analyses calcd (%) for $C_{44}H_{42}N_{14}O_{12}Br_6Zn_5 \cdot DMF$ (1838.36): C 30.71, H 2.69, N 11.43; found: C 30.75, H 3.10, N 11.50; ^{1}H NMR (400 MHz, $[D_6]$DMSO, 22 °C): $\delta = 8.42$ (s, 1 H; H-C=N), 6.98 (dd, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 2.0 Hz, 1 H; H-$C_{(4)}$), 6.91 (d, ^4J(H,H) = 2.0 Hz, 1 H; H-$C_{(6)}$), 6.43 (d, ^3J(H,H) = 9.0 Hz, 1 H; H-$C_{(3)}$).

$[H_6(C_{25}H_{18}N_6O_6Br_3)]Cl$ (5): Triaminoguanidinium chloride (2.007 g, 0.014 mol) was dissolved in a hot mixture of methanol (46 mL), water (62 mL) and hydrochloric acid (pH ~3). A solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (10.852 g, 0.047 mol) in methanol (247 mL) was slowly added. The resulting suspension was allowed to cool to room temperature. The precipitate of **5** was filtrated, washed with diethyl ether and dried under reduced pressure. Yield: 10.227 g (0.013 mol, 92.9 %). Elemental analysis calcd (%) for $C_{25}H_{24}N_6O_6Br_3Cl \cdot 2H_2O$ (815.69): C 36.81, H 3.46, N 10.30; found: C 37.06, H 3.60, N 10.24. ^{1}H NMR (400 MHz, $[D_6]$DMSO, 22 °C): $\delta = 12.07$ (s, 1 H; NH), 9.94 (s, 1 H; OH), 9.05 (s, 1 H; H-C=N), 7.99 (d, ^4J(H,H) = 2.0 Hz, 1 H; H-$C_{(6)}$), 7.22 (d, ^4J(H,H) = 2.0 Hz, 1 H; H-$C_{(4)}$), 3.89 (s, 3 H; OCH_3); ^{13}C NMR (100 MHz, $[D_6]$DMSO, 22 °C) : $\delta = 149.15$ (C^+), 148.75 ($C_{(3)}$), 146.19 (C=N), 146.04 ($C_{(2)}$), 121.26 ($C_{(6)}$), 120.02 ($C_{(1)}$), 116.40 ($C_{(4)}$), 110.78 ($C_{(5)}$), 56.32 (CH_3). Suitable crystals for X-ray structural analysis of **5** were grown by diffusion of HCl gas into a solution of **5** in ethanol.

$(C_6H_{16}N)_{18}[Zn_{30}(C_{25}H_{18}N_6O_6Br_3)_{12}Cl_{12}(\mu\text{-}Cl)_6(H_2O)_6] \cdot x\,CH_3CN \cdot y\,H_2O$ (6): $ZnCl_2$ (82.06 mg, 0.60 mmol) was dissolved in a mixture of acetonitrile (3.6 mL) and DMF (0.4 mL). Tris(5-bromo-2-hydroxy-3-methoxybenzylidene)triaminoguanidinium chloride (131.38 mg, 0.169 mmol) was added. Triethylamine (2.0 mL) was slowly diffused into the reaction mixture. After two weeks, yellow crystals of **6** were formed. Yield: 124.55 mg (0.0093 mmol, 66.0 %). Elemental analysis calcd (%) for $(C_6H_{16}N)_{18}[Zn_{30}(C_{25}H_{18}N_6O_6Br_3)_{12}Cl_{18}(H_2O)_6] \cdot 12\,CH_3CN \cdot 12\,H_2O$ (14114.22): C 36.76, H 4.11, N 10.12; found: C 36.73, H 4.63, N 9.93; ^{1}H NMR (400 MHz, $[D_6]$DMSO, 22 °C) : $\delta = 8.7$–8.3 (4 s, $2+2+12+2$ H; 6×3 H-C=N), 7.7–6.6 (8 d, ^4J(H,H) = 2.0–2.4 Hz, $2+2+2+2+2+12+2+12$ H; 6×3 H-$C_{(4)}$ + 6×3 H-$C_{(6)}$), 3.8–3.7 (2 s, $6+48$ H; 6×3 OCH_3), 2.8 (m, ~55 H; 9×3 CH_2 of Et_3NH^+), 1.2 (m, ~80 H; 9×3 CH_3 of Et_3NH^+).

X-ray analysis (see Table 3): Intensity data for **5** and **6** were collected on an Oxford Diffraction Xcalibur2, for **2** on a Nonius Kappa CCD (rotating anode), for **3** on a STOE IPDS 2 and for **4** on an AXS Smart/CCD diffractometer always using $Mo_{K\alpha}$ radiation and employing the ω scan method. All data were corrected for Lorentz and polarisation effects. Absorption corrections were performed for **4** by SADABS and for **2**, **3**, **5** and **6** by the Gauss method. All structures were solved by using direct methods (SHELXS-97)[11] and refined by using a full-matrix least-squares refinement procedure (SHELXL-97).[12] The protons were placed at geometrically calculated positions. Owing to the large number of disordered solvent molecules (and counter cations in **6**) and the resulting low data-to-parameter ratio we decided to correct the X-ray data of **3**, **4** and **6** by

Table 3. Crystal data for **2**–**6**.

	2	**3**	**4**	**5**	**6**
formula	$(C_{37}H_{53}N_8O_3Br_3Zn_3Cl_6)\cdot 0.5\,C_3H_6O$	$(C_{44}H_{49}N_{19}O_9Br_6Zn_6)\cdot 0.25\,CH_3OH$	$C_{44}H_{42}N_{14}O_{12}Br_6Zn_5$	$(C_{25}H_{24}N_6O_6Br_3Cl)\cdot 2H_2O$	$C_{408}H_{519}N_{90}O_{78}Cl_{18}Br_{36}Zn_{30}$
M_r	1335.45	1867.71	1765.23	815.71	13405.07
crystal size [mm]	0.10×0.09×0.08	0.22×0.22×0.22	0.43×0.22×0.21	0.31×0.24×0.19	0.38×0.24×0.19
crystal system	monoclinic	trigonal	triclinic	monoclinic	triclinic
space group	$C2/c$	$R\bar{3}$	$P\bar{1}$	Cc	$P\bar{1}$
T [K]	100	293	213	100	100
a [Å]	13.560(2)	36.945(5)	17.318(4)	28.286(1)	18.359(2)
b [Å]	24.006(4)	36.945(5)	21.023(4)	16.2256(9)	31.567(3)
c [Å]	32.797(4)	29.605(6)	25.005(5)	14.1171(8)	33.861(3)
α [°]	90	90	88.68(3)	90	69.034(9)
β [°]	95.44(1)	90	86.29(3)	110.845(5)	80.009(9)
γ [°]	90	120	68.24(3)	90	87.097(8)
V [Å^3]	10628(3)	34994(10)	8438(3)	6055.1(6)	18045(3)
ρ_{calcd} [g cm^{-3}]	1.669	1.595	1.390	1.790	1.234
$2\theta_{max}$ [°]	49.56	49.00	50.00	50.50	50.00
data collected	69305	71902	48129	24574	114125
unique data	9062	12919	29262	10378	62394
R_{int}	0.0289	0.1003	0.0803	0.0716	0.1215
observed data [$I > 2\sigma(I)$]	8603	7844	11004	9559	15629
μ [mm^{-1}]	3.944	4.957	4.290	4.143	3.09
T_{min}/T_{max}	0.707/0.768	0.320/0.338	0.314/0.406	0.353/0.610	0.348/0.575
refined parameters	730	783	1459	781	1570
R_1 [$I > 2\sigma(I)$]	0.0671	0.0541	0.0741	0.0414	0.0957
wR_2 (all data)	0.1586	0.1356	0.2066	0.1008	0.2560
residual e$^-$ [e Å^{-3}]	1.224/−1.180	0.801/−0.717	1.459/−1.223	1.333/−0.803	1.443/−0.936

employing the SQUEEZE routine in PLATON.[13] The solvent molecules (and remaining counter cations in **6**) occupy up to 47% of the cell volume (~9100 Å^3 of 34994 Å^3 in **3**, ~3300 Å^3 of 8438 Å^3 in **4** and ~8500 Å^3 of 18045 Å^3 in **6**). Nevertheless the twelve hydrogen-bonded Et_3NH^+ ions of the expected eighteen cations in **6** were located in the difference syntheses and refined. They were all disordered but could be modelled with bond lengths fixed to literature values.

CCDC-257809–CCDC-257813 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors would like to thank Heike Schucht (Max Planck Institut für Bioanorganische Chemie, Mülheim) for the data collection of **2**, Dr. Rolf-Dieter Hoffmann (Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster) for the data collection of **3**, and Annegret Knüfer (Anorganische Chemie I, Ruhr-Universität Bochum) for the data collection of **4**.

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Received: December 8, 2004